

Argonne National Laboratory

PREPARATION OF METALS BY MAGNESIUM-ZINC REDUCTION

Part III. Reduction of Plutonium Dioxide

by

J. B. Knighton and R. K. Steunenberg

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ANL-7059
Chemical Separations
Processes for
Plutonium and Uranium
(TID-4500, 45th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60440

PREPARATION OF METALS BY
MAGNESIUM-ZINC REDUCTION

Part III. Reduction of Plutonium Dioxide

by

J. B. Knighton and R. K. Steunenberg

Chemical Engineering Division

Part I is ANL-7057
Part II is ANL-7058

June 1965

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U. S. Atomic Energy Commission

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	4
I. INTRODUCTION	4
II. EXPERIMENTAL PROCEDURE	5
III. RESULTS	6
A. Flux Composition	6
B. Magnesium Concentration	7
C. Yields and Losses	8
D. Demonstration Experiment	9
IV. DISCUSSION	10
V. CONCLUSIONS	11
ACKNOWLEDGMENT	11
REFERENCES	12

FIGURE

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Distribution of Plutonium between Zinc-Magnesium Alloy and Fluxes Containing Magnesium Chloride	8

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Effect of Flux Composition on the Reduction Rate of Plutonium Dioxide	6
II.	Comparative Reduction Rates of Thorium, Uranium, and Plutonium Oxides	7
III.	Effect of Magnesium Concentration on the Reduction Rate of Plutonium Dioxide	7
IV.	Comparative Analyses of Plutonium Dioxide Starting Material and Plutonium Metal Product	9

INTRODUCTION

Previous investigations had shown that uranium and thorium oxides and sesquioxides (UO_3 , UO_2 , U_2O_3 , ThO_2 , Th_2O_3) are reduced to the corresponding metals or alloys by liquid magnesium-zinc alloy in the presence of suitable fluxes ($CaCl_2$). In view of the successful reduction of these oxides by this method, it is desirable but less extensively studied was attempted the reduction of plutonium dioxide.

The most difficult need for the production of plutonium metal was that of a more reduction of plutonium hexafluoride by Ca with $CaCl_2$ as a flux or a chloride to increase the temperature of the reaction. Although a variety of other reducing agents, including lithium, sodium, potassium, magnesium, calcium, disodium, sodium, and boron, have been used to reduce plutonium oxides and sesquioxides, lithium has been reported to be the most effective ($1,2$). High temperatures of plutonium metal as a metal, however, at various values, but the temperature values are not given. The present work is the first of a series of studies to study the reduction of plutonium dioxide by liquid magnesium-zinc alloy in the presence of suitable fluxes.

PREPARATION OF METALS BY MAGNESIUM-ZINC REDUCTION

Part III. Reduction of Plutonium Dioxide

by

J. B. Knighton and R. K. Steunenber

ABSTRACT

Plutonium metal had been prepared on a laboratory scale by the direct reduction of plutonium dioxide with liquid magnesium-zinc alloy in the presence of fluxes composed of alkali and alkaline earth halides. The reduction rate of plutonium dioxide, unlike those of uranium and thorium oxides, was relatively independent of the flux composition. The most satisfactory reductions at 800°C were obtained with a magnesium concentration of about 10 w/o in the liquid-metal phase. A 30-gram ingot of metallic plutonium was produced by vacuum distillation of magnesium and zinc from the liquid-metal product solutions. The use of plutonium dioxide instead of fluorides as the starting material has the advantage of a greatly decreased neutron-emission hazard resulting from (α, n) reactions. Plutonium losses arising from incomplete reduction in this process were less than 1%.

I. INTRODUCTION

Previous investigations had shown that uranium and thorium oxides and fluorides (U_3O_8 , UO_2 , UF_4 , ThO_2 , ThF_4) are reduced to the corresponding metals in good yield by liquid magnesium-zinc alloy in the presence of a suitable halide flux.^{1,2} In view of the successful reductions of these metals by this technique, a similar but less extensive study was undertaken on the reduction of plutonium dioxide.

The current method used for the production of plutonium metal consists of a bomb reduction of plutonium tetrafluoride by calcium, with iodine added as a booster to increase the temperature of the reaction.³⁻⁷ Although a variety of other reducing agents, including lithium, sodium, potassium, magnesium, barium, aluminum, carbon, and beryllium, have been used to reduce plutonium dioxide and halides, calcium has generally proved to be the most satisfactory.³⁻⁸ Bomb reductions of plutonium dioxide have been attempted at various times, but this procedure yields an unrecoverable powder because the heat of reaction is insufficient to melt the slag.³

Plutonium trichloride can be reduced satisfactorily, but it has the undesirable property of being extremely hygroscopic. Although plutonium tetrafluoride is the most suitable material for the bomb-reduction technique, it has the disadvantage that a substantial neutron flux results from the nuclear reaction $^{19}\text{F}(\alpha, n)^{22}\text{Na}$.

II. EXPERIMENTAL PROCEDURE

The equipment used for the plutonium dioxide reduction studies consisted of a resistance-heated, stainless-steel, tilt-pour furnace² located inside a high-alpha glovebox facility. The reaction was conducted in a tantalum crucible inside a graphite secondary vessel. Provisions were made to measure and control the temperature, to sample the flux and metal phases, and to maintain an argon atmosphere.

To perform a reduction, a charge consisting of zinc, plutonium dioxide, and the desired flux was added to the tantalum crucible at room temperature and heated to 800°C under an argon atmosphere. Mixing was then started, and the magnesium metal was added. The time of magnesium addition was considered to be the starting time of the reduction. Metal samples were then taken after 15, 30, 60, and 120 min by withdrawing the liquid metal through a porous tantalum filter into a tantalum tube. Unfiltered flux samples were taken at 120 min in open-end tantalum tubes.

When the reduction was completed, the molten contents of the tantalum crucible were poured into a graphite mold. After the equipment had cooled overnight, it was disassembled and the flux was separated from the plutonium-magnesium-zinc ingot. The metallic plutonium product was recovered by vacuum distillation of the zinc and magnesium and consolidated by melting.

Except where indicated otherwise, the experimental conditions (temperature, 800°C; mixing rate, 800 rpm; charge size, 300 g of flux and 600 g of zinc-magnesium alloy; atmosphere, argon) were held constant throughout the study. Sufficient plutonium dioxide was used to produce a plutonium concentration of 1.0 w/o in the zinc-magnesium alloy upon complete reduction of the oxide. This plutonium concentration was well below an estimated solubility limit for plutonium in the zinc-magnesium alloy. In one demonstration experiment, enough plutonium dioxide was used to produce 30 g of metallic plutonium.

The zinc and magnesium used in the reductions were of purities greater than 99.999 and 99.95%, respectively. The flux constituents were anhydrous reagent-grade salts, except for the magnesium chloride, which

was anhydrous material obtained from commercial sources as a by-product of the reduction of zirconium tetrachloride by magnesium metal. The plutonium dioxide was standard production-grade material with a plutonium content of 84.1 w/o.

III. RESULTS

A. Flux Composition

The effect of flux composition on the reduction rate of plutonium dioxide was investigated, using a zinc-5 w/o magnesium alloy as the reductant. Five experiments were performed with fluxes that had given both good and poor reductions of uranium and thorium oxides. The results are listed in Table I. Nearly complete reduction of the plutonium dioxide occurred in all cases. Subsequent examination of product ingots showed that the plutonium content of the flux was a more reliable measure of the extent of reduction than that of the filtered metal samples. The flux samples indicated that all of the reductions were at least 99% complete after 120 min. The plutonium concentrations in the metal samples were somewhat low, apparently because a small amount of the plutonium reacted with the tantalum container to form an insoluble plutonium-tantalum inter-metallic compound. Nevertheless, the metal samples were useful in showing that all of the reductions were nearly complete in 30 min or less.

Table I
EFFECT OF FLUX COMPOSITION ON THE REDUCTION RATE
OF PLUTONIUM DIOXIDE

Temperature: 800°C
Mixing Rate: 800 rpm
Metal: 600 g Zn-5 w/o Mg
Flux: 300 g, composition as shown
Oxide: 7.13 g PuO₂

Flux (m/o)	Percent Reduction of PuO ₂ , Metal Samples				Percent of Initial Pu in Flux at 120 min
	15 min	30 min	60 min	120 min	
95.0 MgCl ₂ -5.0 MgF ₂	96	97	93	94	0.5
47.5 CaCl ₂ -47.5 MgCl ₂ -5.0 MgF ₂	95	97	95	97	0.5
47.5 LiCl-47.5 CaCl ₂ -5.0 MgF ₂	-	98	93	-	0.04
47.5 KCl-47.5 CaCl ₂ -5.0 MgF ₂	94	96	96	96	0.2
47.5 KCl-47.5 LiCl-5.0 MgF ₂	-	95	92	94	0.2

The result that the reduction rate was independent of flux composition was unexpected in view of the strong dependence observed in the reductions of uranium and thorium oxides. In particular, magnesium chloride, which was an essential flux ingredient for uranium and thorium

oxide reductions, appeared to contribute nothing to the reduction of plutonium dioxide; it may be a somewhat undesirable constituent. Examples of differences in the reduction behavior of U_3O_8 , thorium dioxide, and plutonium dioxide with various fluxes are illustrated in Table II.

Table II
COMPARATIVE REDUCTION RATES OF THORIUM, URANIUM,
AND PLUTONIUM OXIDES

Flux (m/o)	Percent Reduction in 120 min		
	ThO ₂ ^a	U ₃ O ₈ ^a	PuO ₂ ^b
95.0 MgCl ₂ -5.0 MgF ₂	27.0	99.9+	99+
47.5 LiCl-47.5 CaCl ₂ -5.0 MgF ₂	15.0	56.0	99+
47.5 KCl-47.5 CaCl ₂ -5.0 MgF ₂	No data	21.4	99+
47.5 KCl-47.5 LiCl-5.0 MgF ₂	~3.0	3.0	99+

^aAir atmosphere.

^bArgon atmosphere; results based on flux analyses.

B. Magnesium Concentration

The effect of magnesium concentration in the zinc phase on the reduction of plutonium dioxide was investigated, using a flux consisting of 47.5 m/o CaCl₂, 47.5 m/o MgCl₂, and 5.0 m/o MgF₂. The results are given in Table III. It is not immediately obvious, from the plutonium concentrations in the metal and flux samples, that the magnesium content of the metal phase had a significant effect. However, if these data are expressed

Table III
EFFECT OF MAGNESIUM CONCENTRATION ON THE REDUCTION RATE
OF PLUTONIUM DIOXIDE

Temperature: 800°C
Mixing Rate: 800 rpm
Metal: 600 g Mg-Zn alloy
Flux: 300 g 47.5 m/o MgCl₂-
47.5 m/o CaCl₂-5.0 m/o MgF₂
Oxide: 7.13 g PuO₂

Mg Conc'n. in Zn (w/o)	Percent Reduction of PuO ₂ , Metal Samples				Percent of Initial Pu in Flux at 120 min	$K_d = \frac{\text{w/o Pu in flux}^a}{\text{w/o Pu in metal}}$
	15 min	30 min	60 min	120 min		
1.0	89	89	86	89	2.0	0.045
2.9	92	90	92	88	0.6	0.014
4.7	95	97	95	97	0.6	0.012
9.9	93	90	88	91	0.5	0.011
39.0	87	94	95	89	1.8	0.041
69.2	80	85	80	80	6.5	0.163

^a120-min samples.

as distribution coefficients, $K_d = (w/o \text{ Pu in flux}) / (w/o \text{ Pu in metal})$, it becomes apparent that the most favorable region for plutonium dioxide

reduction is in the vicinity of 10 w/o magnesium, as shown by the minimum of the dashed curve in Figure 1. This curve represents the distribution coefficients as a function of magnesium concentration. Also included in Figure 1 for comparison are two distribution-coefficient curves that were obtained in other work⁸ in which plutonium was equilibrated between liquid magnesium-zinc alloys and magnesium chloride-based fluxes. The minimum at about 10 w/o magnesium is evident in all three curves, and it can be seen that the distribution coefficients increase regularly with increasing concentration of magnesium ion in the flux. Thus, for optimum reduction of plutonium dioxide, a magnesium chloride-free flux would be indicated. In a practical sense, however, this effect is of little importance, since even with a 100% magnesium chloride flux, the plutonium distribution coefficient at 10 w/o magnesium is still sufficiently low for satisfactory reductions.

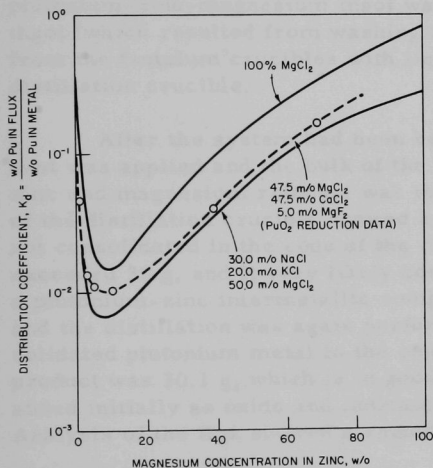
Figure 1

DISTRIBUTION OF PLUTONIUM BETWEEN
ZINC-MAGNESIUM ALLOY
AND FLUXES CONTAINING
MAGNESIUM CHLORIDE

Temperature: 800°C

Mixing Rate: 300 rpm (solid lines)

800 rpm (dotted line)



C. Yields and Losses

The data in Tables I and III are based on a final plutonium concentration of 1.0 w/o in the metal phase upon complete reduction. Material balances, which depend mainly upon the metal samples, showed considerable scatter in the various experiments, and they were biased on the low side. It was suspected, and later confirmed, that the apparent losses resulted from interaction of the metallic plutonium with impurities (probably tantalum) in the metal solution to form insoluble species. This effect was shown in one experiment in which the reduction yield based on the filtered metal sample was 90%, compared to a yield of 99.4% based on the plutonium content of the flux. Analyses of two pie-shaped samples cut from the solidified metal ingot showed that all of the reduced plutonium was present in the metal phase. In general, the results indicate that the plutonium dioxide reduction yields are inherently greater than 99%.

D. Demonstration Experiment

As a final test of the zinc-magnesium reduction procedure, a demonstration experiment was performed in which sufficient plutonium dioxide was used to produce 30 g of plutonium metal upon complete reduction. The charge consisted of a total of 600 g of metal (540 g of zinc and 60 g of magnesium), 300 g of flux (47.5 m/o CaCl_2 -47.5 m/o MgCl_2 -5.0 m/o MgF_2), and 35.65 g of plutonium dioxide (84.1 w/o plutonium). The reactants were heated to 800°C in a tantalum crucible and agitated at 800 rpm for 120 min under an argon atmosphere. At the end of the reduction period, the molten contents of the tantalum crucible were poured into a graphite mold. The plutonium-zinc-magnesium ingot was cleaned and charged along with a zinc ingot (which resulted from washing residual, unpoured, metallic plutonium from the tantalum crucibles with liquid zinc) to a cone-shaped, tantalum distillation crucible.

After the system had been held overnight at 20 microns pressure, heat was applied and the bulk of the zinc was vaporized at 500°C. Final zinc and magnesium removal was then attempted at 700°C. Examination of the distillation crucible showed an irregular metallic product that had not consolidated in the cone of the crucible. The weight of the product exceeded 30 g, and it very likely consisted of a mixture of plutonium and a plutonium-zinc intermetallic compound. More magnesium was added, and the distillation was again performed at 700°C. The result was consolidated plutonium metal in the cone of the crucible. The weight of the product was 30.1 g, which is in good agreement with the amount of plutonium added initially as oxide and indicates complete reduction of the oxide. Analysis of the flux showed a reduction yield in excess of 99%.

A sample of the plutonium product was removed from the ingot and submitted for spectrochemical analysis. A comparison of these results and a spectrochemical analysis of the initial plutonium dioxide is given in Table IV. Apparently, metallic plutonium of good purity can be prepared by this method, although it is suspected that some tantalum, which was not detected by the spectrochemical analysis, might have been present.

Table IV

COMPARATIVE ANALYSES OF PLUTONIUM DIOXIDE STARTING MATERIAL AND PLUTONIUM METAL PRODUCT

Spectrochemical analysis; results in ppm

Element	Plutonium Dioxide	Plutonium Metal	Element	Plutonium Dioxide	Plutonium Metal
Al	180	100	Mn	30	10
B	1	<2	Na	50	<5
Ba	1	<1	Ni	90	25
Ca	140	25	Pb	8	10
Cr	100	1	Sn	<5	10
Fe	100	75	Sr	<0.5	<0.01
K	10	<5	Zn	<5	15
Mg	300	85			

IV. DISCUSSION

The experimental results suggest that the reduction of plutonium dioxide by zinc-magnesium alloy proceeds by a different general mechanism than the reductions of uranium and thorium oxides. For example, plutonium dioxide reduction was much faster, the rate and extent of reduction were practically independent of flux composition, and the final extent of reduction appeared to be limited only by the distribution coefficient of plutonium between the flux and metal phases. In these respects, the plutonium dioxide reductions were more similar to results obtained with uranium and thorium halides than to those obtained with the oxides. As in the case of uranium and thorium, the low activity coefficient of plutonium in zinc-rich solutions contributes to the free energy change of the reduction reaction. The solubility of plutonium in zinc is about 0.4 w/o at 600°C and 9 w/o at 800°C.

The effects of temperature and agitation on the reduction were not investigated specifically. Since the temperature coefficients of the reduction rates of uranium and thorium oxides are small, the temperature of 800°C used in these studies could probably be reduced to 650 or 700°C for the reduction of plutonium dioxide. Effective mixing of the flux and metal phases was essential for satisfactory reduction rates of uranium and thorium oxides, but it may be of less importance in the case of the more easily reducible plutonium dioxide.

Previous work with uranium and thorium halides, together with some other experience with plutonium halides, indicates that the chlorides or fluorides of plutonium should be reduced at least as easily as the oxides. However, one of the advantages of oxide reduction over the use of plutonium tetrafluoride as a starting material is that the neutron emission resulting from (α, n) reactions is greatly diminished. Under optimum conditions, plutonium losses in the liquid-metal reduction procedure should be less than 0.5%, and the indications are that a certain degree of purification is achieved, particularly from electropositive elements such as the alkali and alkaline earth metals.

Although tantalum equipment was used in these studies, other materials would be more suitable for a practical process. Tungsten vessels, for example, have proven to be satisfactory for the reduction of uranium oxide on a 2-kg scale.⁹ Ceramic or ceramic-lined vessels may be desirable for the retorting and product-consolidation step.

V. CONCLUSIONS

The liquid zinc-magnesium reduction procedure appears to have several possible advantages for the production of plutonium metal. Plutonium dioxide is readily reduced by zinc-magnesium alloy. For example, over 99% reduction occurred within 30 min in experiments using 5 to 10 w/o magnesium-zinc alloy. Alloys of higher magnesium concentration resulted in incomplete reductions.

The effect of salt composition on the reduction was not as pronounced as that observed in reductions of U_3O_8 and thorium dioxide. The extent of plutonium dioxide reduction is limited by the distribution coefficient of plutonium between the salt and metal phases. Salts with low magnesium chloride concentrations are preferred, since the plutonium distribution to the salt decreases with decreasing magnesium chloride concentration.

The reagents used in the process are inexpensive, and the zinc and excess magnesium can be recycled. If plutonium dioxide is used instead of fluoride as the starting material, the cost of fluorination is eliminated, and the neutron hazard arising from (α, n) reactions is greatly decreased. Apparently, plutonium metal of good purity can be produced in yields exceeding 99%. Serious consideration of this type of process for the production of metallic plutonium, however, would require considerable additional information to define the optimum conditions and to determine the engineering and economic feasibility.

ACKNOWLEDGMENT

The authors wish to thank J. D. Schilb and J. W. Walsh for their technical assistance, R. P. Larsen and C. Seils for the analytical determinations, and R. C. Vogel and L. Burris, Jr., for their helpful support and counsel.

REFERENCES

1. J. B. Knighton and R. K. Steunenberg, Preparation of Metals by Magnesium-Zinc Reduction. Part I. Reduction of Uranium Oxides, ANL-7057 (June 1965).
2. A. V. Hariharan, J. B. Knighton, and R. K. Steunenberg, Preparation of Metals by Magnesium-Zinc Reduction. Part II. Reduction of Thorium Dioxide, ANL-7058 (June 1965).
3. I. L. Jenkins, N. J. Keen, and A. G. Wain, Alternative Routes for the Conversion of Plutonium Salts to Metal and Their Recovery Problems, in Extractive and Physical Metallurgy of Plutonium and Its Alloys, W. D. Wilkinson, Ed., Interscience Publishers, Inc., New York, p. 25 (1960).
4. R. D. Baker and W. J. Maraman, Calcium Reduction of Plutonium Halides to Metal, ibid., p. 43.
5. F. Anselin, Preparation of Metallic Plutonium, ibid., p. 61.
6. E. Grison, The Preparation of Metallic Plutonium, in Progr. in Nuclear Energy, V, Metallurgy and Fuels, H. M. Finniston and J. P. Howe, Eds., Pergamon Press, New York, p. 91 (1959).
7. O. J. C. Runnalls, The Preparation of Plutonium-Aluminum and Other Plutonium Alloys, ibid., p. 98.
8. S. Fried, E. F. Westrum, Jr., H. L. Baumbach, and P. L. Kirk, The Microscale Preparation and Micrometallurgy of Plutonium, in The Metal Plutonium, A. S. Coffinberry and W. N. Miner, Eds., The University of Chicago Press, Chicago, p. 18 (1961).
9. J. B. Knighton and R. K. Steunenberg, Distribution of Selected Elements Between Magnesium Chloride and Magnesium-Zinc Alloy, Trans. Am. Nucl. Soc. 5(2), 460 (1962).
10. L. Burris, Jr., I. G. Dillon, and R. K. Steunenberg, The EBR-II Skull Reclamation Process. Part I. General Process Description and Performance, ANL-6818 (Jan 1964).

ARGONNE NATIONAL LAB WEST



3 4444 00007722 2

2